PECVD of SiO_x Films with Electron Beam Generated Plasmas

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ABSTRACT

Plasma enhanced chemical vapor deposition (PECVD) processes open up wide parameter spaces compared to CVD techniques, most notably the lowering of substrate temperatures. Furthermore, modulated plasma systems can provide even greater control over the deposition conditions by tailoring a gas phase – surface phase synergy to achieve optimum growth conditions for the desired films.

We have formulated a PECVD process in an electron beam generated plasma to deposit silicon-based dielectric films tailored to display applications on flexible substrates (low temperature, low damage). These plasmas provide an ideal platform for film deposition, such as low electron temperature/ion energy (reduced film damage), high plasma density (high flux of reactive species), and uniform chemical activation of the gas (controllable gas phase chemistry). This work discusses the recent progress on the PECVD of SiO_x films using pulsed electron beam generated plasmas with an organic precursor (TEOS). The film characteristics are compared with complementary flux measurements from *in situ* mass spectrometry.

INTRODUCTION

Dielectric thin films continue to be used in applications from nanometer-scale electronic device gates to multi-layer optical coatings for architectural glazings. Hence, as the composition of materials and their critical properties are nearly as limitless as the applications. The fabrication of these materials has become more complex with the advancement of applications, not just because of the variety of materials, but also the variety of substrates. Instead of glass substrates, polymeric materials that are lighter, cheaper and safer to use are desired, but fabrication techniques have to be modified, if not replaced, to accommodate the new substrate's thermal and physical damage thresholds.

Plasmas generated by high energy e-beams have a large potential as next-generation plasma processing systems due to their highly localized, uniform ionization region and their ability to be scaled to very large areas while maintaining an open geometry for substrates. These plasmas have demonstrated high densities ($n_e = 10^9$-10^{12} cm^{-3}) in a variety of gases while maintaining a low temperature plasma ($T_e \leq 0.5$ eV). The low electron temperatures translate to low plasma potentials and ion energies (< 3 eV). Additional details of these systems can be found elsewhere in these proceedings [1].

With the versatility afforded by the plasma system, a plasma enhanced chemical vapor deposition (PECVD) arrangement was studied to determine process feasibility. The use of the broader chemistry capabilities, tunable ion energies and modulation of the plasma source during deposition were investigated.

EXPERIMENT

The system used in the present experiments was identical to previous work [2] so only details specific to the PECVD process are given here. A -2 kV/2 ms electron beam (e-beam) was operated with a 10 ms period (20% duty factor typical) and collimated by a 165 G magnetic field over the length of the chamber. Substrates (p-type <100> silicon) were mounted on the processing stage 2.5 cm from the edge of the electron beam. Reference [1] shows a typical arrangement for the present experiments.

Tetraethyl orthosilicate (TEOS) was introduced by flowing 10 sccm of argon through a room temperature bubbler kept at 18 Torr by a throttle valve between the bubbler and a gas feed tube that extended to the stage. Argon (40 sccm) and oxygen (50 sccm) were introduced through the system sidewall with no special relation to the substrate or e-beam. A total flow of 100 sccm was used in all cases. For the gas flows mentioned above, the individual flows were calculated to be 2/48/50 sccm of TEOS/Ar/O_2, respectively. These flows and the 20% duty factor were the 'standard conditions' used in experiments. Exposure time was the total time that the plasma was on; thus the laboratory time would be the exposure time divided by the duty factor (0.2 for standard conditions).

A pretreatment plasma (20% duty factor, 50 sccm each of Ar and O_2) was run for 4-5 minutes of exposure time before each deposition. For deposition, the TEOS/Ar/O_2 gas flows were adjusted accordingly, which increased the operating pressure from 52 to approximately 55 mTorr. After the deposition, a plasma post-treatment identical to the pre-treatment was carried out.

To increase the incident ion energy, rf (13.6 MHz) power was synced to the e-beam duration and applied to form an rf induced dc bias on the stage front. The applied peak-to-peak rf voltage

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(V^{rf}_{pp}) was measured at the stage power feedthrough with an oscilloscope probe and was kept constant during deposition. V^{rf}_{pp} was set to 50 V for the pre/post treatment phases of the ion energy experiments.

Ex situ measurements of film thickness (white-light spectrophotometer and/or profilometry) chemical composition (FTIR), porosity (wet etching) and smoothness (AFM) were carried out. To compare steady-state film compositions [3,4] most FTIR analyses shown here were carried out after a week of exposure to laboratory air. Wet etching was done in a P etch solution [5] of $15HF:10HNO_3:300H_2O$ (by volume).

Flux composition and ion energy distributions were determined using a quadrupole mass spectrometer (Hiden EQP300) as discussed in Reference [6]. Ions and neutrals were sampled through a 100 micron orifice in the center of a stainless steel electrode located 1.2 cm from the beam edge. Ion flux measurements were time resolved with standard gating techniques [7] over a 3 ms window that included the entire e-beam pulse and 1 ms of the afterglow. Neutral measurements were obtained by operating the EQP300 in RGA mode with the first element after the orifice biased positive to repel plasma ions and the ionizer energy set to 70 eV. Standard mass and energy resolutions were 0.2 amu and 0.15 eV, respectively; spectra were not corrected for mass transmission efficiencies.

RESULTS & DISCUSSION

Mass Spectrometry

The ion energy distributions of the Ar/O_2 pretreatment plasma are shown in Figure 1a, scaled to the O_2^+ signal. These distributions show very well behaved structures with low mean energies centered around 1.25 eV. The temporal evolution of these ion fluxes to the stage are shown in Figure 1b. These results were obtained by summing over all of the ion energies. From Figure 1b, it can be seen that the atomic ions (Ar^+, O^+) rapidly decay after the e-beam pulse, likely due to charge-exchanging ion molecule reactions with the molecular oxygen species: $Ar^+ + O_2 \rightarrow Ar + O_2^+$, $k = 5 \times 10^{-11}$ cm^3/s^1; $O^+ + O_2 \rightarrow O + O_2^+$, $k = 2 \times 10^{-11}$ cm^3/s. The molecular oxygen ions, aside from being generated by the atomic ions, decay at a slightly slower rate, according to dissociative recombination with the remaining plasma electrons: $O_2^+ + e \rightarrow O_2$, $k(cm^3/s) \sim 2x10^{-8}/[T_e(eV)]^{0.56}$.

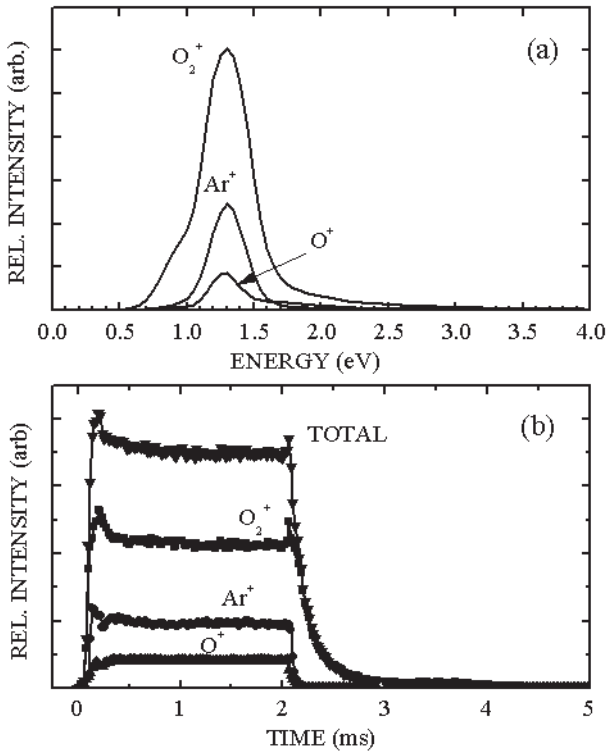

Figure 1: (a) Ion energy distribution functions from an Ar/O_2 e-beam generated plasma. (b) Temporal evolution of plasma ion species.

The ion mass spectrum for the standard deposition mixture is shown in Figure 2. The dominant ion at the surface was still O_2^+, but the other species were H_3O^+ (50%), H_2O^+ (27%), $C_2H_5^+$ (20%) and Ar^+ (19%). (The numbers in parentheses give the relative intensities with respect to the O_2^+ signal.) The decline of the O^+ and Ar^+ species in this spectrum and the appearance of H_3O^+ and H_2O^+ imply that the plasma ions underwent additional ion-molecule reactions with the deposition by-product, water. The rates for these reactions are quite high ($k \sim 10^{-9}$ cm^3/s) and are expected to be rapid near the source (surface). Higher mass peaks are present up to the parent molecule in very low quantities (< 1%) (see inset).

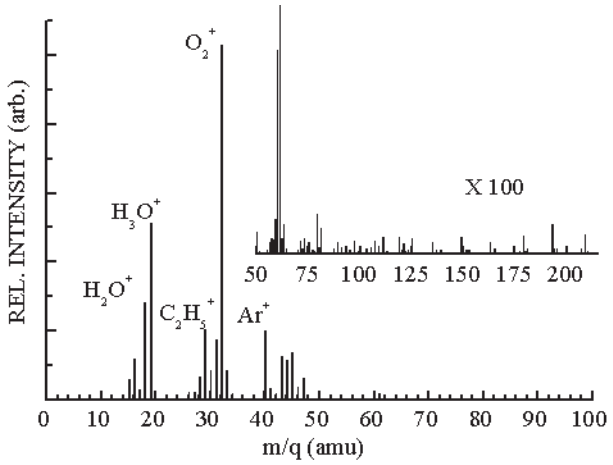

Figure 2: Ion mass spectrum from TEOS/Ar/O_2 e-beam generated plasma.

Figure 3 shows the neutral mass spectra on a semi-logarithmic scale. Although difficult to discern, both the m/q=44, 18 (CO_2, H_2O, respectively) peaks increased by nearly a factor of 2 and the m/q=28 (CO, Si) peak increased by a factor of 4 when the plasma was on, whereas the O_2 concentration decreased slightly with the plasma on. Thus the presence of the plasma significantly altered the background gas concentration (due to the aforementioned ion-molecule reactions). The reaction by-products (CO, CO_2) are all liberated from the surface and also can be ionized by the plasma, thereby giving rise to water peaks in the ion mass spectrum of Figure 2.

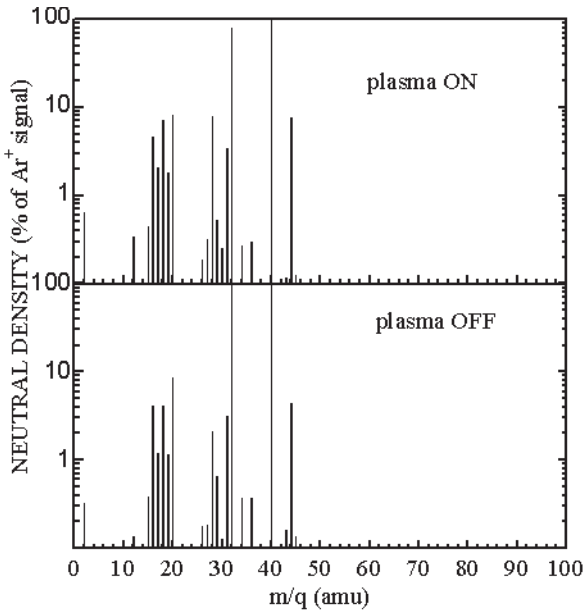

Figure 3: Neutral mass spectrum from TEOS/Ar/O_2 e-beam generated plasma.

Plasma Chemistry

At a surface temperature of 300 °C and a grounded substrate, the growth rate of SiO_x film increased nearly linearly with the flow of TEOS, while the film composition showed an incorporation of silanol (SiOH) groups in the film (Figure 4). The typical Si-O-Si bonding peaks were seen (1070 cm^{-1} stretch with shoulder, 812 cm^{-1} bend and 450 cm^{-1} rock) in all films as well as the SiO-H stretch (3650 cm^{-1}) due to isolated silanol groups. As the TEOS concentration in the gas mixture increased, a second SiO-H stretch peak attributed to the interaction of neighboring silanol groups appeared at 3450 cm^{-1}. Hence, additional silanol groups were incorporated into the film with increased precursor flow. It is important to point out that from the present experiments it cannot be determined if the films were formed with additional silanol groups or the films hydrolyzed upon removal from vacuum. When oxygen was removed from the gas mixture, the growth rate dropped dramatically while the chemical etch rate similarly increased, and the film showed the presence of aliphatic chains (C-H stretch at 2950 cm^{-1}) (Figure 5). In addition, another silanol peak appeared (SiO-H bend at 933 cm^{-1}) as the O_2 flow decreased. For both of these chemistry variations, the etch rates increased with the appearance of these additional peaks in the FTIR, impling that more porous films were made when the TEOS flow was high and when the oxygen flow was eliminated. These observations are consistent with a precursor-mediated growth mechanism [8]: in order to react, the TEOS molecule had to adsorb on the surface first; then the molecule is oxidized by the reactive plasma species (atomic oxygen) to first form SiOH, then SiO_2. Excess TEOS flow resulted in the precursor not being fully reacted; (shown by the increased presence of SiOH groups) while eliminating the oxygen prevented the first process, the removal of the organic chains of the precursor. Thus, the film's insufficient oxidation process trapped both silanol and aliphatic groups in the film. Consequently, the film porosity (wet chemical etch rates) escalated rapidly as there was insufficient oxygen species to react with the precursor.

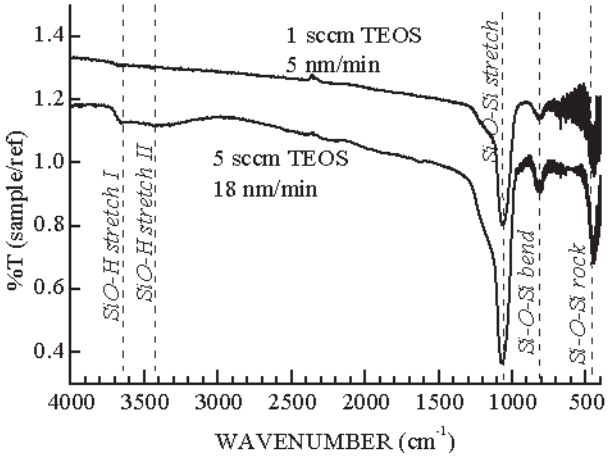

Figure 4: FTIR spectra of films grown at various TEOS flows. Growth rates are given under flow labels.

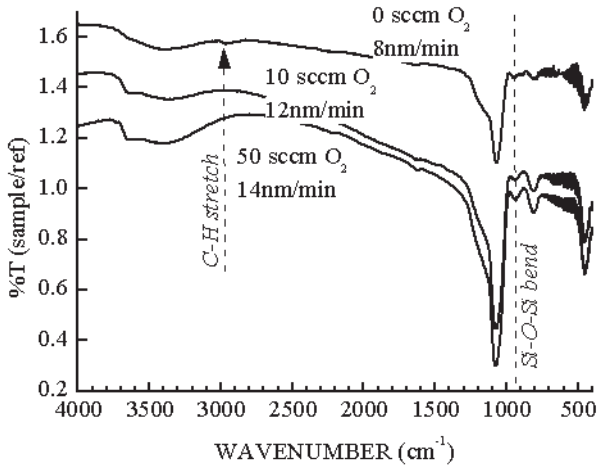

Figure 5: FTIR spectra of films grown at various O_2 flows. Growth rates are given under flow labels.

The changes in film growth and etch rates as the plasma duty factor was varied at the standard conditions are shown in Figure 6. From these dependencies there was a critical 'plasma off' time for the 20% duty factor. For this case, the plasma was off for 8 ms, which is very close to the atomic oxygen diffusion time in the PECVD system (≈ 7 ms). Thus, at increased off times (lower duty factors) there would be a diminished flux of O atoms to react, while shorter off times (higher duty factors) would basically receive a sufficient O atom flux to react with the constantly adsorbing precursor molecules.

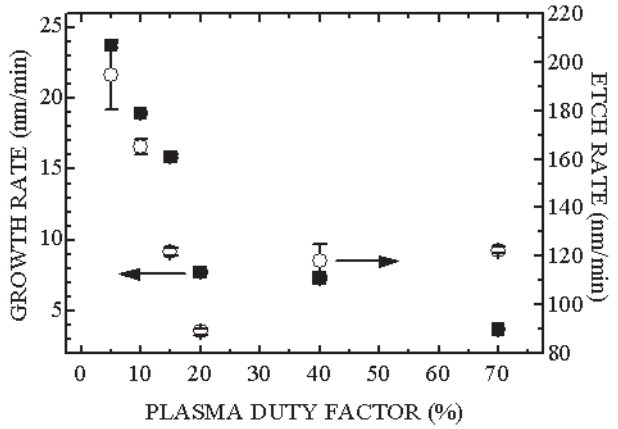

Figure 6: Growth (solid) and etch (open) rates of films at various duty factors.

Ion energy

In Figure 7 the growth and etch rates are plotted for V^{rf}_{pp} settings ranging from 0 to 100 V. During these experiments, the V^{rf}_{pp} voltages were kept constant as well as the rf power delivered to the stage, and the substrate temperature was kept at 200°C. Table 1 gives the average steady-state value of the dc voltage $<V^{rf}_{pp}>$ induced by the applied V^{rf}_{pp}. The growth rates increased rapidly with the increasing incident ion energy as the etch rate correspondingly decreased.

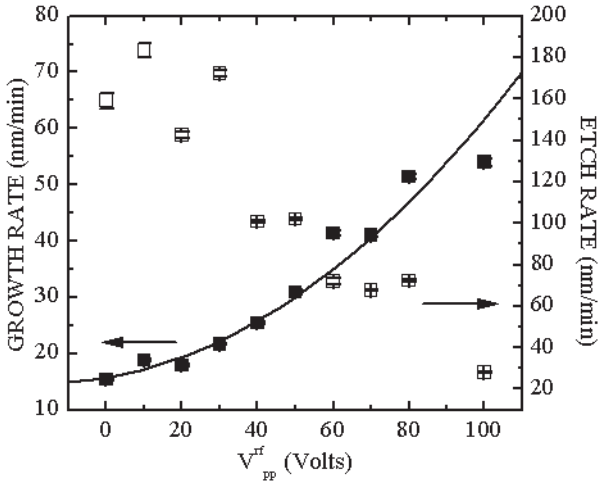

Figure 7: Etch (solid) and growth (open) rates of films grown at various applied rf voltage levels.

Table 1: Ion energy ($<V^{rf}_{pp}>$), stage power and film roughnes for applied rf voltage levels (V^{rf}_{pp}).

V^{rf}_{pp}(V)	$<V^{rf}_{pp}>$ (V)	Power (mW/ cm^2)	RMS rough. (nm)
100	-47	147	1.24
90	-42	131	0.875
80	-36	113	0.901
70	-31	95	0.763
60	-24	70	0.692
50	-17	39	--
40	-13	21	0.506
30	-11	11	--
20	-7.5	5	0.458
10	-4.5	1	--

The time evolutions of the FTIR spectra of films grown at various ion energies are shown in Figure 8. Most notably in these spectrum are the evolution of the peaks due to collective interaction between SiOH groups (3450 and 933 cm^{-1}) and the consistent presence of the isolated SiOH group peak (3650 cm^{-1}). As the incident ion energy was increased, the evolution of the collective SiOH groups was delayed, until it ceased to appear at V^{rf}_{pp} = 70 V. Thus stable films were produced when the ion energy was above 24 eV (V^{rf}_{pp} = 60 V) and for lower ion energies, film composition could change significantly with time. From these results, it appeared that the films grown at lower energies were subject to attack by ambient water due to a strained O-Si-O bond formation of the SiO_2 lattice [3].

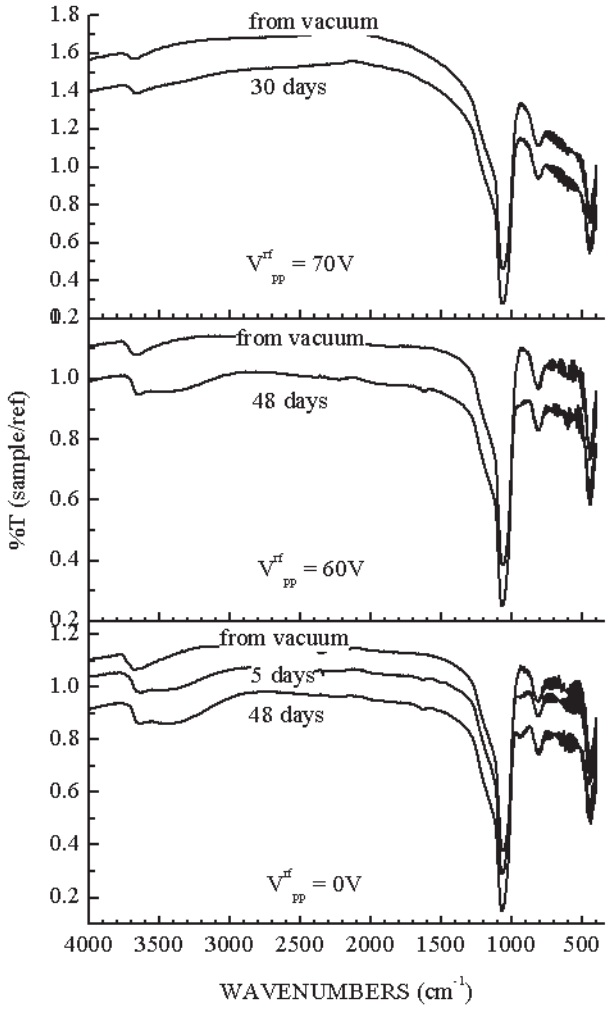

Figure 8: Evolution of film compositions by FTIR analysis for various values of V^{rf}_{pp}.

In addition to reducing the occurrence of the silanol groups, increased ion energies also resulted in smoother films, also listed in Table 1. Above V^{rf}_{pp} = 40 V, the final film possessed an RMS roughness that was smoother than the substrate (RMS roughness of 0.686 nm). Further increases of the rf voltage (and subsequent ion energy) continued to decrease the film roughness as well.

CONCLUSION

Electron beam generated plasmas have demonstrated a significant degree of process control in a PECVD system utilizing TEOS precursor to form SiO_x films. In addition to general processing parameters of gas composition and substrate temperature, more convoluted parameters of duty factor, ion flux and energy were also investigated. These factors have shown a strong influence over the formation of usable dielectric films, especially the ion energy, including the time evolution of the film once removed from vacuum.

ACKNOWLEDGEMENT

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